THERMAL DIFFUSION IN LIQUIDS ON THE SURFACE OF A ROTATING DISK

(UDC 533.735)

V. G. Levich, V. S. Markin, and Yu. G. Chirkov

Institute of Electrochemistry, Academy of Sciences, USSR

Translated from Élektrokhimiya, Vol. 1, No. 12,
pp. 1416-1421, December, 1965
Original article submitted April 19, 1965

A calculation was made of the thermal diffusion currents during an arbitrary type of chemical or electrochemical reaction on the surface of a disk electrode. An explicit expression is given for the currents for first order reactions. The expressions obtained made it possible to determine the Soret coefficient in liquids.

Reliable measurement of the Soret coefficient, thermal diffusion coefficients in liquids, is an extremely difficult experimental task. In the majority of published works a direct method is used for this purpose. A solution is placed in a cell between two plates having a temperature difference. Owing to thermal diffusion a concentration gradient arises in the solution. Various methods were suggested for measuring this gradient, including optical [1-4] and electrical [5-9]. Indirect thermal gravitational methods [10] were also used, one of the variations of which is the electrothermal diffusion method [11, 12]. Laying aside the question of the comparative accuracy of these methods, it should be noted that all of them possess a very substantial disadvantage: the presence of a temperature gradient inevitably causes natural convection which mixes the solution. As a result, measurements of extremely small Soret coefficients are not very reliable. A method is discussed below, in which natural convection does not affect the measurements of the Soret coefficients. The method is based on the use of a rotating disk electrode. The rotating disk electrode was proposed as a device for electrochemical measurements by one of us [13] in 1943. Thanks to the works of A. N. Frumkin and his followers the disk electrode has become one of the most often used devices for electrochemical investigations.

We will consider a disk with a temperature T_0 rotating in a solution with a concentration c_∞ and temperature T_∞. One of us [13] has determined the distribution of the dissolved substance on the surface of the rotating disk and the current of substance to the disk in the isothermal case. The temperature distribution on the disk rotating in a homogeneous liquid was calculated by Kibel' with consideration of the heat liberated as a consequence of dissipation [14]. If dissipation is ignored, then the temperature distribution will become unidimensional and similar to the concentration distribution. The surface of the disk we will consider to be infinitely large, ignoring edge effects. In this case the whole surface of the rotating disk is equally accessible in a diffusional sense. This circumstance made the rotating disk very convenient for studying heterogeneous reactions, in particular electrochemical reactions, reactions connected with solution, etc. The equally accessible nature of the surface of the rotating disk makes it, evidently, a convenient instrument for investigating the thermal diffusion phenomena in liquids.

The presence of two gradients at once complicates the problem since in the expressions for the currents cross terms [15] appear, and the equations prove to be linked. We will write the dissolved-substance current and the heat flow relative to the liquid in the following form:

$$\mathbf{J}_c = -D\nabla c - Dsc\nabla T, \tag{1}$$

$$\mathbf{J}_T = -\varkappa\nabla T - d\nabla c. \tag{2}$$

Here D is the diffusion coefficient, $\varkappa$ the thermal conductivity coefficient, s the Soret coefficient, and d the Dufour coefficient. The last terms in these formulas describe, respectively, the Soret effect, or thermal diffusion, and the Dufour effect.

In general, it is necessary to write a supplementary multiplier of the type $(1-c)$ in the thermal diffusion term. However, in the case of not too high concentrations it can be approximately replaced by one.

Distribution of the substance and temperature in the stationary case in the absence of energy dissipation is determined by the system of equations:

$$\mathbf{v}\nabla c = -\nabla \mathbf{J}_c, \tag{3}$$

$$\rho c_p \mathbf{v}\nabla T = -\nabla \mathbf{J}_T. \tag{4}$$

If there occurs on the surface of the disk a chemical or electrochemical reaction, the rate of which is given by the function $f(c_0)$, where c_0 is the concentration on the surface of the disk, then the boundary conditions have the form:

$$|\mathbf{J}_c(0)| = f(c_0), \qquad c(\infty) = c_\infty, \tag{5}$$

$$T(0) = T_0, \qquad T(\infty) = T_\infty. \tag{6}$$

Here ρ is the density and c_p the specific heat of the solution, y the coordinate reckoned from the surface of the disk to the depth of the solution, v is the velocity of the stream entrained by the disk [16, 17, 13].

The Dufour effect in liquids is very small [15]. The temperature gradient affects the distribution of the substance via thermal diffusion, which is very small in comparison with the normal convective diffusion. As a result changes introduced into the concentration by the Dufour effect will be still smaller and they can not be examined. We will attempt to find a solution for the formulated boundary problem considering the concentration as depending only on the distance to the surface of the disk:

$$\begin{cases} \mathrm{v}_y \dfrac{dc}{dy} = D\dfrac{d^2c}{dy^2} + Ds\dfrac{d}{dy}c\dfrac{dT}{dy} & (7) \\[2ex] \mathrm{v}_y \dfrac{dT}{dy} = \chi\dfrac{d^2T}{dy^2}, & (8) \end{cases}$$

where χ is the thermal diffusivity. In the future it will be convenient to use the dimensionless variable

$$\xi = y(\omega / \nu)^{1/2}. \tag{9}$$

The quantities ω and ν denote, respectively, the angular rotational velocity of the disk and the kinematic viscosity. In such dimensionless variables Eqs. (7) and (8) will assume the form:

$$c'' - \frac{\nu}{D}Hc' = -s\frac{d}{d\xi}(cT'), \tag{10}$$

$$T'' - \frac{\nu}{\chi}HT' = 0. \tag{11}$$

The function $H(\xi)$ is given in [16, 17, 13]. The system (3)-(4) is unlinked to the above assumptions. Solution of Eq. (11) with the boundary condition (6) has the form [13]:

$$T(\xi) = \frac{T_\infty - T_0}{\beta}\int_0^\xi L^{\nu/\chi}(\eta)\,d\eta + T_0, \tag{12}$$

$$L(\eta) = \exp\left[\int_0^\eta H(\xi)\,d\xi\right], \tag{13}$$

$$\beta = \int_0^\infty L^{\nu/\chi}(\eta)\,d\eta. \tag{14}$$

Integral (14) has been evaluated by various authors [13, 18-20]. The values of the integrals β for a series of values of ν/χ are presented below [20].

ν/χ	0.01	0.1	1.0	10.0	100.0
β	114.87	13.058	2.524	0.882	0.372

As a rule, the Soret coefficient s for aqueous solutions is in the range from 10^{-1} to 10^{-2} $\deg^{-1}$. The smallness of this quantity makes it possible to solve Eq. (10) practically without restriction of its generality by the following approximate means. Distribution of the substance in the first approximation is determined by solving Eq. (10) without the right hand portion with the boundary conditions (5) [13]:

$$c^0(\xi) = \frac{c_\infty - c_0{}^0}{\alpha} \int\limits_0^\xi L^{\nu/D}(\eta)\,d\eta + c_0{}^0, \tag{15}$$

where, with an accuracy above 1% [19],

$$\alpha = \int\limits_0^\infty L^{\nu/D}(\eta)\,d\eta = 1,61 \left(\frac{D}{\nu}\right)^{1/3} \left[1 + 0,35 \left(\frac{D}{\nu}\right)^{0,36} \right]. \tag{16}$$

The constant c_0^0 is found from the boundary condition [5]. For finding the next approximation, the solution of (15), we will substitute in the right hand portion of Eq. (10):

$$c'' - \frac{\nu}{D} H c' = -\frac{s(T_\infty - T_0)}{\beta} \frac{d}{d\xi} \left\{ \left[\frac{c_\infty - c_0{}^0}{\alpha} \int\limits_0^\xi L^{\nu/D}(\eta)\,d\eta + c_0{}^0 \right] L^{\nu/\chi}(\xi) \right\}. \tag{17}$$

The general solution of Eq. (17) is the function:

$$\begin{aligned} c(\xi) = {} & a \int\limits_0^\xi L^{\nu/D}(\eta)\,d\eta + b + \frac{s(T_\infty - T_0)\,c_0{}^0 D}{\beta(\chi - D)} \int\limits_0^\xi L^{\nu/\chi}(\eta)\,d\eta \\ & - \frac{s(T_\infty - T_0)(c_\infty - c_0{}^0)\chi}{\alpha\beta(\chi - D)} \int\limits_0 L^{\nu/D}(\eta)\,d\eta \int\limits_0 L^{\nu/\chi}(\xi)\,d\xi \\ & + \frac{s(T_\infty - T_0)(c_\infty - c_0{}^0) D}{\alpha\beta(\chi - D)} \int\limits_0^\xi L^{\nu/\chi}(\eta)\,d\eta \int\limits_0^\eta L^{\nu/D}(\xi)\,d\xi. \end{aligned} \tag{18}$$

The constants a and b are found from the boundary conditions (5).

As an example we will examine a heterogeneous first order chemical or electrochemical reaction. In other words we will postulate that the density of the current j on the surface of the disk is related to the concentration by the expression:

$$j = k(T_0)\,c_0. \tag{19}$$

The rate constant k depends on the temperature T_0 on the surface of the disk, and in the case of an electrochemical reaction also on the electrode potential. For a first order reaction the boundary conditions (5) take the form:

$$\begin{gathered} Dc'|_{\xi=0} + DscT'|_{\xi=0} = (\nu/\omega)^{1/2} k(T_0)\,c(0), \\ c(\infty) = c_\infty. \end{gathered} \tag{20}$$

For this case the constant c_0^0 is found in [13]:

$$c_0{}^0=\frac{Dc_\infty}{k(T_0)\alpha(\nu/\omega)^{1/3}+D}. \tag{21}$$

Finding the arbitrary constants a and b in the general Eq. (18) will lead to solution of the system of equations:

$$Da+[Ds(T_\infty-T_0)/\beta-(\nu/\omega)^{1/3}k(T_0)]b=-s(T_\infty-T_0)c_0{}^0D^2/[\beta(\chi-D)], \tag{22}$$

$$\alpha a+b=c_\infty-\frac{s(T_\infty-T_0)c_0{}^0D}{\chi-D}$$

$$+\frac{s(T_\infty-T_0)(c_\infty-c_0{}^0)\chi}{\alpha\beta(\chi-D)}\int\limits_0^\infty L^{\nu/D}(\eta)\,d\eta\int\limits_0^\eta L^{\nu/\chi}(\xi)\,d\xi$$

$$-\frac{s(T_\infty-T_0)(c_\infty-c_0{}^0)D}{\alpha\beta(\chi-D)}\int\limits_0^\infty L^{\nu/\chi}(\eta)\,d\eta\int\limits_0^\eta L^{\nu/D}(\xi)\,d\xi. \tag{23}$$

The second integral in (23) will lead to the first:

$$\int\limits_0^\infty L^{\nu/\chi}(\eta)\,d\eta\int\limits_0^\eta L^{\nu/D}(\xi)\,d\xi=\alpha\beta-\int\limits_0^\infty L^{\nu/D}(\xi)\,d\xi\int\limits_0^\xi L^{\nu/\chi}(\eta)\,d\eta. \tag{24}$$

For convenience of calculation of the first integral we will divide it into two parts:

$$\int\limits_0^\infty L^{\nu/D}(\eta)\,d\eta\int\limits_0^\eta L^{\nu/\chi}(\xi)\,d\xi=\int\limits_0^\infty \eta L^{\nu/D}(\eta)\,d\eta$$

$$-\int\limits_0^\infty L^{\nu/D}(\eta)\,d\eta\int\limits_0^\eta\left(1-L^{\nu/\chi}(\xi)\right)d\xi. \tag{25}$$

For calculation of the first term we will use the first two terms of the expansion H(ξ) at small distances. As was shown in [13], this can be done since the ratio ν/D is very large. Then for the integral γ we have the expression

$$\gamma=\int\limits_0^\infty \eta L^{\nu/D}(\eta)\,d\eta\cong\int\limits_0^\infty \eta\exp\left\{-\frac{\nu}{D}\left(0,17\eta^3-\frac{1}{12}\eta^4\right)\right\}d\eta$$

$$\cong\int\limits_0^\infty\left[\eta+\frac{1}{12}\,\frac{\nu}{D}\eta^5\right]\exp\left\{-\frac{\nu}{D}0.17\eta^3\right\}d\eta=1.47(D/\nu)^{2/3}+0.96(D/\nu). \tag{26}$$

We will show that in comparison with the first term the second term in (25) can be ignored. For this we will use the obvious inequality $1-e^{-x}\leq x$. Then

$$\int\limits_0 L^{\nu/D}(\eta)\,d\eta\int\limits_0^\eta\left(1-L^{\nu/\chi}(\xi)\right)d\xi\leqslant-\frac{\nu}{\chi}\int\limits_0^\infty L^{\nu/D}(\eta)\,d\eta\int\limits_0^\eta\left[\int\limits_0^\xi H(\varphi)\,d\varphi\right]d\xi$$

$$\cong\frac{\nu}{\chi}\,\frac{0.17}{4}\int\limits_0^\infty\eta^4L^{\nu/D}(\eta)\,d\eta=0.04\frac{\nu}{\chi}\int\limits_0^\infty\eta^4\exp\left(-0.17\frac{\nu}{D}\eta^3\right)d\eta$$

$$=0.013\frac{\nu}{\chi}\left(\frac{D}{0.17\nu}\right)^{5/3}\Gamma(5/3). \tag{27}$$

For aqueous solutions the latter value is 0.1% of γ. By substituting (24) and (26) in (23) we will find the following expressions for a and b with an accuracy up to that of the main terms:

$$a = \frac{c_\infty - c_0{}^0}{\alpha} + s(T_\infty - T_0)\left\{\frac{c_\infty - c_0{}^0}{\alpha}\,\frac{c_0{}^0}{c_\infty}\left(\frac{\alpha}{\beta} - \frac{D}{\chi}\right)\right.$$

$$\left. + \frac{(c_\infty - c_0{}^0)^2}{\alpha c_\infty}\left(\frac{\gamma}{\alpha\beta} - \frac{D}{\chi}\right) - \frac{c_0{}^0}{\beta}\right\}, \tag{28}$$

$$b = c_0{}^0 + s(T_\infty - T_0)\left\{-\frac{(c_0{}^0)^2}{c_\infty}\left(\frac{\alpha}{\beta} - \frac{D}{\chi}\right)\right.$$

$$\left. + \frac{c_0{}^0(c_\infty - c_0{}^0)}{c_\infty}\left(\frac{\gamma}{\alpha\beta} - \frac{D}{\chi}\right)\right\}. \tag{29}$$

The density of the current taken from the disk equals

$$j = j_0\left\{1 + s(T_\infty - T_0)\left[\frac{c_0{}^0}{c_\infty}\left(\frac{\alpha}{\beta} - \frac{D}{\chi}\right) + \frac{c_\infty - c_0{}^0}{c_\infty}\left(\frac{\gamma}{\alpha\beta} - \frac{D}{\chi}\right)\right]\right\}, \tag{30}$$

where

$$j_0 = k(T_0)\,c_0{}^0. \tag{31}$$

Let us examine the limiting cases of very slow and very rapid reactions. In the case of a very slow reaction (formally, the transition $k \to 0$ corresponds to this) the value of c_0^0 differs very little from that of c_∞. Therefore, we obtain

$$j = j_0\left[1 + s(T_\infty - T_0)\left(\frac{\alpha}{\beta} - \frac{D}{\chi}\right)\right]. \tag{32}$$

In the case of a very rapid reaction (formally, $k \to \infty$) the concentration on the disk equals zero and the current attains the limiting value

$$j_{\lim} = j_0\left[1 + s(T_\infty - T_0)\left(\frac{\gamma}{\alpha\beta} - \frac{D}{\chi}\right)\right]. \tag{33}$$

It should be noted that the formula for the limiting current does not depend on the kinetic law for a surface reaction and is valid for any order reaction.

In conclusion we will indicate the numerical values of the characteristic constants. For aqueous solutions under normal conditions $\nu/\chi = 6.75$, $\nu/D \cong 10^3$, $\alpha = 0.19$, $\beta = 1.64$, $\gamma = 0.016$.

LITERATURE CITED

1. C. C. Tanner, Trans. Faraday Soc., 23, 75 (1927).
2. C. C. Tanner, Trans. Faraday Soc., 49, 611 (1953).
3. J. Chanu and J. Lenoble, J. chim. phys. et phys.-chim. biol., 53, 309 (1956).
4. L. G. Longsworth, J. Phys. Chem., 61, 1557 (1957).
5. J. Chipman, J. Amer. Chem. Soc., 48, 2577 (1926).
6. J. N. Agar and W. G. Breck, Trans. Faraday Soc., 53, 167 (1957).
7. J. N. Agar and J. C. R. Turner, J. Phys. Chem., 64, 1000 (1960).
8. P. N. Snowdon and J. C. R. Turner, Trans. Faraday Soc., 56, 1409, 1812 (1960).
9. A. D. Payton and J. C. R. Turner, Trans. Faraday Soc., 58, 55 (1962).
10. K. F. Alexander, Z. phys. Chem., 203, 213 (1954).

11. B. Baranowski, Bull. Acad. Pol. Sci., Cl. III, 2, 439 (1954).
12. B. Baranowski and J. Demichowicz, Bull. Acad. Pol. Sci., Cl. III, II, 435 (1954).
13. V. G. Levich, Physicohemical hydrodynamics [in Russian], Moscow, Fizmatgiz (1959).
14. S. Z. Kibel', Prikl. matem. i mekhan., 11, 611 (1947).
15. S. R. de Groot, Thermodynamics of irreversible processes [Russian translation], Moscow, GITTL (1956).
16. Collection: Contemporary problems of hydrodynamics, Vol. 1 [in Russian], Moscow, Izd. Inostr. Lit. (1948), p. 122; T. Karman, Z. angew. Math. u Mech., 1, 244 (1921).
17. W. G. Cochran, Proc. Cambridge Phylos. Soc., 30, 365 (1934).
18. K. Millsaps and K. Pohlhausen, J. Aeronaut Sci., 19, 120 (1952).
19. D. P. Gregory and A. C. Riddiford, J. Chem. Soc., No. 10, 3756 (1956).
20. E. M. Sparrow and J. L. Gregg, Trans. ASME, ser. C, 81, 249 (1959).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.